Thermodynamics

Remedial Lecture 4

03 – 10 – 2022

Course outline

- 5 sessions:
  - 1 Basics, (state) functions, ideal gas, internal energy, work, heat, Enthalpy
  - 2 Energy, Entropy
  - 3 Energy, chemical reactions
  - **4 Electrochemistry**
  - 5 Colligative properties & statistical thermo

Course today

- Definitions

- Goals of today:
  - To understand what electrochemical/redox reactions are
  - To be able to give all redox reactions
  - To be able to calculate with Nernst law
  - Know the difference between E terminal and E cell
  - Calculations involving reactions in electrochemical cells

Study material

- ~~Study guide (page ….. & .~~.)
- Atkins (see study guide)
- Relevant formulas on formula sheet

$$E = E^{\ominus} - \frac{RT}{\nu F} \ln Q \quad \text{and} \quad \mathrm{d}W' = E\mathrm{d}q$$

$$\mu_i = \mu_i^{\ominus} + RT \ln a_i = \mu_i^{\ominus} + RT \ln \frac{P_i}{P^{\ominus}}$$

$$E = IR \quad \text{and} \quad P = EI$$

- Not on sheet but useful:
  - $\eta = R_L/(R_L + R_i)$

Gibbs free energy and electrochemical cells

Electrochemical cell p,T constant:

$$\Delta_r G = -\nu F \Delta E_{cell}$$

ν:	number of transferred electrons (according to the chemical equation)
F:	Faraday constant = 96 485 C/mol
ΔE_{cell} :	electromotive force of the cell in Volt

If a process is spontaneous then: $\mathbf{\Delta_r G \leq 0}$ (p,T constant)

So for a battery:

$\mathbf{\Delta E_{cell} \geq 0}$ (p,T constant)

Electrical Work

- There is only one formula for electrical work

$$\mathrm{d}W' = E\mathrm{d}q$$

- Be aware of units:
  - W’ in (M)J/mol
  - E in Volt, which is J/C
  - Thus q must be in Coulomb/mol (often 1 Faraday is used.
    - 1 F = 96 485 C/mol

How to construct a chemical half reaction yourself

- put the formula of the particle that reacts on the left hand side, and the formula of the particle that appears on the right hand side of the equation
- put coëfficiënts in front of these formulas, to make sure all elements - except H and O - are equally present before and after the arrow
- equal the missing **O-atoms** with **H_2O**
- equal the missing **H-atoms** with **H^+**
- equal the **charge** with **e^-**
- check the environment:
  - if it is neutral, there can't be any **H^+ ions** present on the left hand side of the equation
  - if it is basic, there can't be any **H^+ ions** present on any side of the equation

In both cases, add as much **OH^- ions** as you need to neutralize the **H^+ ions** to form **H_2O**.
Don't forget to add the same amount of **OH^- ions** on the other side of the equation!

Example questions

Give the half equation for the following half reactions:

1. Copper will become copper(II+) in acidic environment
2. Glucose will become carbondioxide in alkaline environment
3. Ethane-amine will become carbondioxide and nitrogen in neutral environment

Standard conditions

$$\Delta_r G^\ominus = -\nu F \Delta E_{cell}^\ominus$$

oxidizing agent		reducing agent	$E^\ominus$ (V)
$Cu^{2+} + 2\ e^-$	→	Cu	+ 0.34
$2\ H^+ + 2\ e^-$	→	H_2	0.000000
$Zn^{2+} + 2\ e^-$	→	Zn	- 0.76

Redox table
T = 298 K, $p = p^\ominus$ and
all activities a = 1

Standard Daniell cell: Zn(s) | Zn^{2+} || Cu^{2+} | Cu(s)

$\Delta E_{cell}^\ominus = 0.34 - (-0.76) = 1.10$ V

$\Delta_r G^\ominus = -2 \cdot 96485 \cdot 1.10 = -2.12 \cdot 10^5$ J mol^{-1} < 0

Cell notation of n electrochemical cell (a battery), no electrolysis:

- Your electrodes will be on the utmost left hand side and utmost right hand side
- The left hand side will always be the reducing agent (oxidizing reaction at the anode)
- From your electrode to the electrolyte (a phase change) will be a: | sign
- Electrolytes in the same phase will be seperated with a semicolon
- A saltbridge or semi-permeable membrane will be depicted as: ||

Example:
Pt | Fe^{2+}(1M),Fe^{3+}(1M) ‖ Cl_2(g)|Cl^{-}(1M) | Pt

Question
Given the reaction: $2Cr^{3+} + 7H_2O + 3Br_2(l) \rightarrow Cr_2O_7^{2-} + 14H^{+} + 6Br^{-}$

Give the cell notation for this reaction in a electrochemical cell with platina electrodes

$$\mathrm{Pt}|\mathrm{Cr_2O_7^{2-}, Cr^{3+}, H^+} \parallel \mathrm{Br^-} \mid \mathrm{Br_2(l)}|\mathrm{Pt}$$

Non-standard conditions

If $p \neq p^{\Theta}$ and/or $a \neq 1$, apply a correction:

For each electrode: $\mathrm{Ox} + \nu\, \mathrm{e}^- \longrightarrow \mathrm{Red}$

$$E = E^{\Theta} - \frac{\mathrm{R}T}{\nu \mathrm{F}} \ln Q$$

E: potential of the electrode

Q refers to the half-reaction of the cell

For overall potential:

$$\Delta E_{\mathrm{cell}} = \Delta E_{\mathrm{cell}}^{\Theta} - \frac{\mathrm{R}T}{\nu \mathrm{F}} \ln Q$$

Q: reaction quotient

(similar to concentration quotient)

Example: the nickel chromium battery

$Ni^{2+} + 2e^- \rightarrow Ni$ 3x

$Cr \rightarrow Cr^{3+} + 3e^-$ 2x

ν = 6 and $$Q = \frac{a_{Ni}^{3} \cdot a_{Cr^{3+}}^{2}}{a_{Cr}^{2} \cdot a_{Ni^{2+}}^{3}} = \frac{a_{Cr^{3+}}^{2}}{a_{Ni^{2+}}^{3}}$$

If the activities are known you can calculate the potential by:

$$\Delta E_{\text{cell}} = \Delta E_{\text{cell}}^{\Theta} - \frac{\mathrm{R}T}{\nu \mathrm{F}} \ln Q$$

Explanation for nickel chromium battery

$$E = E^{\ominus} - \frac{RT}{\nu F}\ln Q \qquad \Delta E_{cell} = E_{+pole} - E_{-pole}$$

$$E_{+pole} = E^{\ominus}_{+pole} - \frac{RT}{\nu F}\ln\frac{a_{red}}{a_{ox}} = -0.25 - \frac{RT}{2F}\ln\frac{1}{a_{Ni^{2+}}}$$

$$E_{-pole} = E^{\ominus}_{-pole} - \frac{RT}{\nu F}\ln\frac{a_{red}}{a_{ox}} = -0.74 - \frac{RT}{3F}\ln\frac{1}{a_{Cr^{3+}}}$$

$$\Delta E_{cell} = \left(-0.25 - \frac{RT}{2F}\ln\frac{1}{a_{Ni^{2+}}}\right) - \left(-0.74 - \frac{RT}{3F}\ln\frac{1}{a_{Cr^{3+}}}\right)$$

$$\Delta E_{cell} = \left(-0.25 + \frac{RT}{2F}\ln a_{Ni^{2+}}\right) - \left(-0.74 + \frac{RT}{3F}\ln a_{Cr^{3+}}\right)$$

$$\Delta E_{cell} = -0.25 + 0.74 - \left(\frac{RT}{6F}\ln a^{2}_{Cr^{3+}} - \frac{RT}{6F}\ln a^{3}_{Ni^{2+}}\right)$$

$$\Delta E_{cell} = 0.49 - \frac{RT}{6F}\ln\frac{a^{2}_{Cr^{3+}}}{a^{3}_{Ni^{2+}}}$$

$$\Delta E_{cell} = \Delta E^{\ominus}_{cell} - \frac{RT}{\nu F}\ln Q$$

fill in for the reduction reaction:
the terms together and because $y \cdot \ln(b) - y \cdot \ln(c) = y \cdot \ln(b/c)$
By changing the quotients the − ln becomes + ln
$\{y \cdot \ln(x) = y/2 \cdot \ln(x^2)\}$
Fill in $\Delta E_{cell} = E_{+pole} - E_{-pole}$

$Ni^{2+} + 2e^- \rightleftarrows Ni$

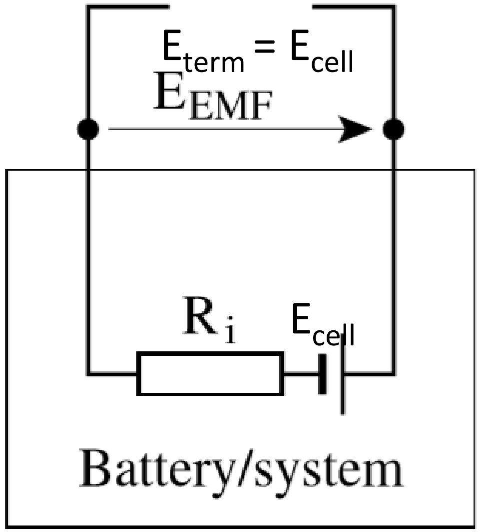
$Cr^{3+} + 3e^- \rightleftarrows Cr$

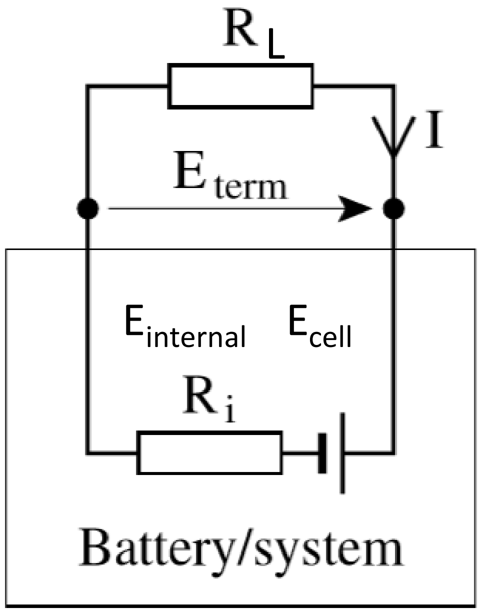
$Ni^{2+} + 2e^-$	$\rightarrow Ni$	3x
Cr	$\rightarrow Cr^{3+} + 3e^-$	2x

$3\,Ni^{2+} + 2\,Cr \rightarrow 3\,Ni + 2\,Cr^{3+}$

Batteries and internal resistance

- Internal resistance is the resistance inside the battery. E_{term} is the voltage over the battery terminals
- When I = 0, $E_{term} = E_{cell}$
  - E_{cell} is also called E_{EMF}
- When I > 0, there is an internal resistance of the battery,
  - $E_{term} = E_{cell} - E_{internal.}$
    - with $E_{internal} = I*R_{internal}$ and $E_L = I*R_L$





The EMF of a battery is 20 V. If one connects a resistance R between the terminals of the battery the potential difference becomes 19 V at a current of $I = 2.5$ A.
Choose the battery as the system.

a) Calculate the external resistance by using Ohm's law: $E = IR = \left(\frac{\mathrm{d}q}{\mathrm{d}t}\right) R$.

b) Calculate the internal resistance of the battery.

c) We let the battery, with the resistance R connected, deliver current isothermally and isochorically for a while. The total charge transfer in this process is 1.0 Faraday.
Calculate the work done by the battery.

d) Calculate the work done by the battery if we let this battery produce 1.0 Faraday of charge isochorically, isothermally and reversibly by loading it with an infinitely high resistance, or during an infinite amount of time.

e) What is the maximum work the battery can do per mole of transferred electrons?

a) The (external) resistance is $R = \frac{E_{term}}{I} = \frac{19}{2.5} = 7.6\ \Omega$. see figure 1.

b) R_i is the internal resistance that causes a decrease of the terminal voltage $E_{term} = E_{EMF} - IR_i \Rightarrow R_i = \frac{E_{EMF}-E_{term}}{I} = \frac{20-19}{2.5} = 0.40\ \Omega$;

c) The transferred charge per mole of electrons is $\Delta q = 1$ F(araday) $= N_A e = 9.6485 \cdot 10^4$ C (e is the elementary charge).
As long as the process is isochoric ($\mathrm{d}V = 0$) there is no mechanical (volume) work. Besides, for such an electrochemical process even under isobaric conditions ($\mathrm{d}P = 0$) we can assume that there is no volume change so that there is no mechanical (volume) work done. So the only work is electrical and at (the given) constant terminal voltage.
If we choose the battery as system, then the system does (electrical) work on the surroundings (the resistance R), or $W < 0$.
In that case $W = -\int E_{term}\mathrm{d}q = -E_{term}\int \mathrm{d}q = -E_{term}\Delta q = -19 \cdot 96485 = -1.83$ MJ/mol.

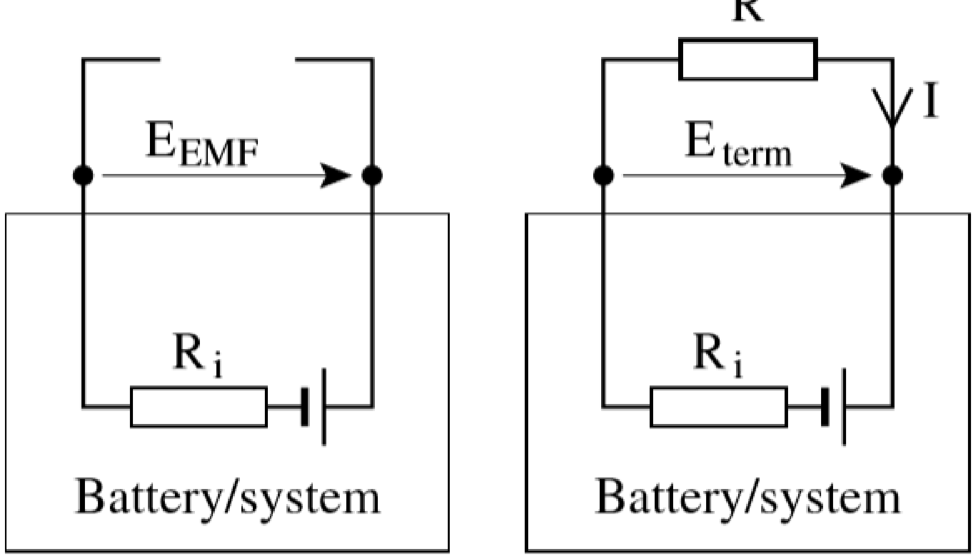


Figure 1: The battery is the system; if there is no external resistance, then the terminal voltage is equal to the maximum voltage of the battery E_{EMF}; if a resistance R is connected the terminal voltage drops with an amount of IR_i to a value of E_{term}.

If we take the external resistance as system then this work is done by the surroundings (battery) on the resistance and is $W = 1.83$ MJ/mol, so positive.

d) Moreover, if the process proceeds reversibly with an infinitely high external resistance, the process indeed takes infinitely long, but $E_{term} = E_{EMF}$, since the current is infinitely small. The work then becomes $W = -\int E_{EMF}\mathrm{d}q = -E_{EMF}\Delta q = -20 \cdot 96485 = -1.93$ MJ/mol.

e) The maximum terminal voltage is $E_{EMF} = 20$ V, so the maximum work per mole of transferred electrons is $W = -\int E_{EMF}\mathrm{d}q = -E_{EMF}\Delta q = -20 \cdot 96485 = -1.93$ MJ/mol, or the work in case the battery delivers current reversibly.

Of course there is a practical limit here, since the E_{EMF} is only realized for (very) small currents, so for a very small amount of power per time unit.

Nernst law

Calculations with Nernst law

Exercise 13

We consider a NiCd-battery at $T = 298$ K. This is a battery that is rechargeable due to a smartly designed cathode and anode, for which the reaction products stick to the electrodes during the discharge.
The redox reaction is in an *aqueous* basic environment, between Cd(s) and $Cd(OH)_2$(s) with a standard potential $E^{\ominus}_{Cd} = -0.81$ V and between NiO_2(s) and $Ni(OH)_2$(s), with a standard potential $E^{\ominus}_{Cd} = 0.49$ V. These (standard) potentials are in the tables of Atkins specified for the half reactions written as *reduction* half reactions, *i.e.* with the electrons on the left hand side in the chemical equation.

a) Write out the chemical equations for the reactions occurring at the two electrodes as *reduction* half reactions as well as the chemical equation for the net cell reaction.
Note that the molalities of the ions in the two half cells need not be the same.

b) Write out the Nernst equation for the potentials of the two half cells and for the cell voltage as far as possible in terms of the potentials and activities, without plugging in the known values.

c) Determine the cell voltage under standard conditions.

a) For rechargeable batteries the notions anode and cathode refer to different electrodes depending on whether the battery is charged or discharged.
Make a distinction between the activities of the ions in the two half cells.
Reduction half reactions always have the electrons on the left hand side in the chemical equation, so we write.

$$\mathrm{NiO_2(s) + 2H_2O(l) + 2e^- \leftrightarrows Ni(OH)_2(s) + 2OH^-_{\mathit{Ni}}(aq)}$$

$$\mathrm{Cd(OH)_2(s) + 2e^- \leftrightarrows Cd(s) + 2OH^-_{\mathit{Cd}}(aq)}$$

Now, the net cell reaction depends on whether we charge or discharge the battery. We choose the following net reaction and we do not know yet, whether this will correspond to charging or discharging

$$\mathrm{NiO_2(s) + 2H_2O(l) + Cd(s) + 2OH^-_{\mathit{Cd}}(aq) \leftrightarrows Ni(OH)_2(s) + Cd(OH)_2(s) + 2OH^-_{\mathit{Ni}}(aq)}$$

b)

$$E_{Ni} = E^{\ominus}_{Ni} - \frac{RT}{\nu F} \ln Q_{Ni} = E^{\ominus}_{Ni} - \frac{RT}{\nu F} \ln \frac{a_{\mathrm{Ni(OH)_2}} a^2_{\mathrm{OH^-},Ni}}{a_{\mathrm{NiO_2}} a^2_{\mathrm{H_2O}}}$$

$$E_{Cd} = E^{\ominus}_{Cd} - \frac{RT}{\nu F} \ln Q_{Cd} = E^{\ominus}_{Cd} - \frac{RT}{\nu F} \ln \frac{a_{\mathrm{Cd}} a^2_{\mathrm{OH^-},Cd}}{a_{\mathrm{Cd(OH)_2}}}$$

The net reaction of part a) then corresponds to a cell voltage of

$$E = E^{\ominus}_{Ni} - E^{\ominus}_{Cd} - \frac{RT}{\nu F} \ln Q_{\mathrm{cell}} = E^{\ominus}_{Ni} - E^{\ominus}_{Cd} - \frac{RT}{\nu F} \ln \frac{a_{\mathrm{Ni(OH)_2}} a_{\mathrm{Cd(OH)_2}} a^2_{\mathrm{OH^-},Ni}}{a_{\mathrm{NiO_2}} a^2_{\mathrm{H_2O}} a_{\mathrm{Cd}} a^2_{\mathrm{OH^-},Cd}}$$

c) At standard conditions the activities of all components are equal to 1 and the cell voltage is

$$E = E^{\ominus}_{Ni} - E^{\ominus}_{Cd} = 0.49 - (-0.81) = 1.30\ \mathrm{V}.$$

d) The initial state of the half cell is represented by a given molality b_i for the ions and we write the corresponding activities in terms of the activity coefficient γ_i on the molality scale according to $a_i = \gamma_i b_i / b^\ominus$.
Assume that the molalities of the ions in the solvent are so low that, still, $a_{H_2O(l)} \approx 1$.
As a (rough) approximation, we now assume that the activity coefficients are independent of the molality.
Determine the cell voltage at a hydroxide molality of 0.01 mol/kg in the cathode half cell and 0.1 mol/kg in the anode half cell; what can you conclude about the change as compared to the voltage under standard conditions?

e) Determine the cell voltage at a hydroxide concentration of 0.1 mol/kg in both half cells and besides that standard conditions; what is your conclusion?

f) Check whether the cell will produce a spontaneous current when a load (resistance) is connected across the cell terminals for the situations of subproblem d) and e).

d) Use that the activity of solid and liquid components is to a good approximation equal to 1. For higher molalities this will be a rough approximation for the solvent.
An even more rough approximation is chosen to assume the activity coefficients to be independent of the molality.
In both reactions two electrons are transferred ($\nu = 2$).

$$E_{Ni} = E^{\ominus}_{Ni} - \frac{RT}{\nu F} \ln Q_{Ni} = 0.49 - \frac{8.315 \cdot 298}{2 \cdot 96485} \ln \frac{1 \cdot a^2_{\mathrm{OH}^-,Ni}}{1 \cdot 1}$$

$$E_{Cd} = E^{\ominus}_{Cd} - \frac{RT}{\nu F} \ln Q_{Cd} = -0.81 - \frac{8.315 \cdot 298}{2 \cdot 96485} \ln \frac{1 \cdot a^2_{\mathrm{OH}^-,Cd}}{1}$$

The net reaction of part a) then corresponds to a cell voltage of

$$E = E^{\ominus}_{Ni} - E^{\ominus}_{Cd} - \frac{RT}{\nu F} \ln Q_{\mathrm{cell}} = E^{\ominus}_{Ni} - E^{\ominus}_{Cd} - \frac{RT}{2F} \ln \frac{a^2_{\mathrm{OH}^-,Ni}}{a^2_{\mathrm{OH}^-,Cd}} = E^{\ominus}_{Ni} - E^{\ominus}_{Cd} - \frac{RT}{F} \ln \frac{a_{\mathrm{OH}^-,Ni}}{a_{\mathrm{OH}^-,Cd}}$$

We assume that γ_i is independent of b_i, such that

$$E = E^{\ominus}_c - E^{\ominus}_a - \frac{RT}{F} \ln \frac{\gamma_{\mathrm{OH}^-} b_{\mathrm{OH}^-,Ni}}{\gamma_{\mathrm{OH}^-} b_{\mathrm{OH}^-,Cd}} = 1.30 - \frac{8.315 \cdot 298}{96485} \ln \frac{0.01}{0.1} = 1.359 \text{ V}$$

So this is a small change in the cell voltage for a factor 10 change in molality between the two half cells.

e)

$$E = E_c^{\ominus} - E_a^{\ominus} - \frac{8.315 \cdot 298}{96485} \ln \frac{0.1}{0.1} = 1.30 \text{ V}$$

As the Nernst equation for this redox couple shows, an equal molality change in the two half cells has no effect on the cell voltage as compared to the standard cell voltage.

f) For both cases the cell voltage is positive, $E > 0$, so $\Delta_r G < 0$, so the reaction will progress spontaneously and therefore a current will be produced.